

S/N 10/751,091

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

|             |  |                 |                |
|-------------|--|-----------------|----------------|
| Applicant:  | MOECKLY ET AL.   | Examiner:       | P. WARTALOWICZ |
| Serial No.: | 10/751,091   | Group Art Unit: | 1793           |
| Filed:      | JANUARY 2, 2004  | Docket No.:     | 10467.43US12   |
| Title:      | HIGH TEMPERATURE SUPERCONDUCTOR DEVICES AND<br>METHODS OF FORMING THE SAME |                 |                |

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**DECLARATION OF JOHN M. ROWELL UNDER 37 C.F.R. 1.132**

I, John M. Rowell, state and declare as follows:

1. I am a Research Professor in the School of Materials at the Arizona State University.
2. I hold a Ph.D. (1961), an M.A. (1961) and a B.A. (1957) in physics from Oxford University.
3. I joined Bell Laboratories in 1961 after carrying out my graduate studies at Oxford University. I held a series of management positions at Bell Laboratories and became Director of the Chemical Physics Laboratory in 1981.
4. In 1963, with P. W. Anderson, I made the first observation of the Josephson Effect and demonstrated the magnetic field sensitivity of the Josephson current. The observation was published in P. W. Anderson and J. M. Rowell, "Probable Observation of the Josephson Superconducting Tunneling Effect", *Phys. Rev. Lett.* 10, 230-232 (1963).
5. In 1966, I obtained what I believe to be the first patent (U.S. 3,281,609) granted for logic applications of the Josephson Effect.

Attachment A

6. With W.L. McMillan, I developed tunneling spectroscopy, a measurement technique that determines in detail the electron-phonon interaction that causes superconductivity, at least in the low-T<sub>c</sub> materials.

7. In collaboration with J. Geerk, M. Gurrvitch and M. Washington, I invented the trilayer niobium/aluminum process that is now the basis of all low-T<sub>c</sub> digital electronics and magnetic sensors.

8. In 1978, I received the Fritz London Memorial Low Temperature Physics Prize for this work on the Josephson Effect, tunneling and superconductivity.

9. In 1983, just prior to the divestiture of the Bell System, I joined Bell Communications Research (Bellcore) as Assistant Vice President, Solid State Science and Technology. I was responsible for guiding the growth of this laboratory from its beginning, including both personnel and facilities. The technical programs of the laboratory included materials research, optoelectronics, optical switching, high speed electronics and high-T<sub>c</sub> superconductivity.

10. In 1989, I joined Conductus, a start-up superconducting electronics company, as its Chief Technical Officer and served as its President for the year of 1991.

11. I have been a consultant specializing in applied superconductivity and the superconductor industry since 1995.

12. In 1997, I was appointed as the Materials Institute Professor at Northwestern University.

13. I have served on a number review boards and committees, including, for example, at the National Science Foundation, and have testified before Congress on research and technology funding issues.

14. I am a Fellow of the American Physical Society, of the American Association for the Advancement of Science, and a Fellow of the Royal Society. I am a member of the National Academy of Sciences and of the National Academy of Engineering.

15. I have reviewed (a) the U.S. Patent Application Serial No. 10/751,091 ("the '091 application"); and (b) K. Harada, H. Myoren, and Y. Osaka, "Fabrication of all-high- $T_c$  Josephson junction using as-grown  $YBa_2Cu_3O_x$  thin films," *Jap. J. Appl. Phys.*, vol. 30, pp. L1387-89 (1991) ("the Harada paper").

16. With my experience as outlined above, I am familiar with the subject matters of the '091 application and the Harada paper.

17. The '091 application discloses a high- $T_c$  Josephson junction in which a barrier between the two high- $T_c$  superconductor layers is made by Argon-Oxygen ion-treatment of a thin surface layer of one of the superconductor layers and thus native to that superconductor layer. The ion treatment process disclosed in the illustrative embodiments in the '091 application resulted in a uniform, reproducible, high-quality barrier, as evidenced by the consistencies in the critical current ( $I_c$ ) and normal resistance ( $R_n$ ) values shown in Figure 6 of the '091 application and high values of the product  $I_c R_n$  (0.3 to 5 mV at 4.2K) for the Josephson junctions.

18. It should be noted that in the process disclosed in the illustrative embodiments of the '091 patent, the Ar-O ion-treatment step for forming the barrier layer is performed *in situ* following the formation of the edge surface of the first superconductor layer by Ar ion milling and annealing. See, the specification at page 11, lines 13 through 20. Therefore, one can be certain that the subsequent Ar-O ion-

treatment step acts on a clean edge surface layer of the superconductor layer, and that the barrier is a modified layer of the superconductor layer.

19. The Harada paper reports a Josephson junction formed between two high- $T_c$  superconductor layers. To form the junction, an insulating film of amorphous YSZ is deposited on the bottom superconductor layer. A portion of the insulating film is subsequently removed by the lift-off technique to expose a surface area of the bottom superconductor layer. The exposed area is then treated with an Ar-O plasma. The top superconductor layer is then deposited over the treated area. See, Figure 2 and associated text at page L1388 of the Harada paper.

20. Although the process reported in the Harada paper apparently resulted in a Josephson junction, the Josephson junction is of very poor quality, as evidenced by an  $I_c R_n$  product of only  $12\mu V$ , which is over an order of magnitude lower than disclosed in the '091 application. The Harada paper also does not demonstrate any reproducibility of the Josephson junction. Such a poor-quality Josephson junction could simply be due to a poor contact, or a contaminated interface, between the two superconductor layers and not necessarily a barrier that is an ion-modified surface layer of the bottom superconductor layer.

21. The statements in the paper are also ambiguous regarding the nature of the barrier: On the one hand, the paper contends that a barrier without grain boundary or insulating films was formed by the plasma treatment; on the other hand, the paper states that the "plasma treatment is very important since the surface layer of the base electrodes may be contaminated and/or have other nonsuperconducting phases." (p. L1388 of the Harada paper.) It is therefore not clear from the Harada paper whether the reported

plasma treatment was intended to modify the bottom superconductor layer or merely to clean its surface.

22. Furthermore, according to the Harada paper, the surface of base electrode is exposed using a "lift-off" technique. Because such techniques involve using solvents to dissolve the insulating layer and photoresist, the exposed surface is typically contaminated. It is therefore not clear that the plasma treatment reported in the Harada paper was acting on a clean surface of the superconductor. The Harada paper therefore does not necessarily show that the barrier was made of an ion modified surface layer of the superconductor layer.

23. In sum, it is not clear from the Harada paper that a barrier made of an ion-modified surface layer of a high-T<sub>c</sub> superconductor was produced. The Josephson junction reported in the Harada paper is significantly inferior to those disclosed in the '091 patent, and simply experimenting with the process reported by the Harada paper would not have lead to the Josephson junction disclosed in the '091 patent.

All statements made of my own knowledge are true, and all statements made on information and belief are believed to be true. Furthermore, I make these statement with the understanding that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and may jeopardize the validity of the application or any patent issuing thereon.

Dated: 4/24/08

John M. Rowell  
John M. Rowell

# Properties of interface-engineered high $T_c$ Josephson junctions

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We have created YBCO thin film ramp edge Josephson junctions by modification of the edge surface prior to counterelectrode deposition. No deposited interlayer or barrier layer is employed. These devices are uniform and reproducible, and they display resistively shunted junction current-voltage characteristics with excellent magnetic field modulation.  $I_c R_n$  values over the range 0.5–3 mV and corresponding  $R_n A$  values of  $6 \times 10^{-8}$ – $1.2 \times 10^{-9} \Omega \text{ cm}^2$  at 20 K are easily attained by varying the process. We believe these junctions offer significant promise as the building blocks of a high  $T_c$  electronics technology. © 1997 American Institute of Physics.  
[S0003-6951(97)02443-1]

Successful implementation of a high  $T_c$  circuit technology based on Josephson devices requires the reproducible fabrication of junctions with appropriate values of key electrical properties as well as a suitably small spread of these parameters. It appears essential to have nonhysteretic critical currents ( $I_c$ s) in the range 100–500  $\mu\text{A}$ , normal resistance ( $R_n$ ) values of one to several ohms, and inductances of several pH, with 1  $\sigma$  spreads in  $I_c$  less than 10% for a minimum of 100 junctions. Other important requirements are the ability to operate in a reasonable temperature range (10–77 K) and the capability of flexible junction placement on the circuit chip. In addition, a slow, nonexponential variation of  $I_c(T)$  is desirable in order to increase the temperature range of operation and reduce the spread in  $I_c$ . Thus far, simultaneous satisfaction of these requirements has proven elusive.

The two looming difficulties of the  $S/\text{interlayer}/S$  devices are control of the  $S/\text{interlayer}$  interface and control of the structural and electrical properties of the interlayer. In most high  $T_c$  superconductor-normal-superconductor (SNS)-type junctions made to date,  $R_n$  of the device is clearly inconsistent with the value of resistivity of the interlayer. It has been shown that this excess resistance occurs at the interface<sup>1</sup> and most likely arises from oxygen sublattice disorder<sup>2,3</sup> caused by thermal and lattice-expansion mismatches. For the case of doped YBCO barriers,<sup>4,5</sup> however, the excess interface resistance has been reduced to less than  $10^{-10} \Omega \text{ cm}^2$ , leading to observation of what may be a true proximity effect device. Indeed, YBCO edge junctions based on Co-YBCO barriers represent the state of the art in terms of reproducibility and uniformity.<sup>6,7</sup> However, the Co-YBCO junctions made at Conductus have the drawback of intrinsically low values of  $R_n$  (typically a fraction of an ohm), which demands high values of  $J_c$  for a useful  $I_c R_n$  product. A high-resistivity barrier material is thus required. Unfortunately, the ability to controllably deposit lattice-matched, high-resistivity, pinhole-free layers on the scale of a few nm (the barrier thickness must decrease with increasing barrier resistivity) is presently beyond our capability and would demand significant advances in our materials science knowledge of these compounds.

We have thus pursued an approach to edge junction for-

mation based on the *elimination of a deposited interlayer*. We believe this will alleviate complications related to deposition of doped-YBCO materials.<sup>8</sup> Drawing on lessons learned from elimination of problems at the  $S/\text{interlayer}$  interface,<sup>1,9</sup> in the present work, we used the interfacial properties to our advantage. Different phases of YBCO have vastly different electrical properties. In loose analogy with the oxidation process used in low  $T_c$  tunnel junctions,<sup>10</sup> our goal was to reliably modify, either chemically or structurally, the exposed YBCO edge prior to deposition of the YBCO counterelectrode, thereby forming a type of *intrinsic* barrier free of the problems of deposited layers and complex compounds. This idea was catalyzed by the results of experiments we undertook to anneal YBCO films, which showed that the whole of an orthorhombic film could be easily converted to a cubic phase simply by appropriate low-temperature vacuum annealing.<sup>11</sup> We have also recently become aware of and encouraged by work which has indicated that ion plasma treated YBCO surfaces may lead to Josephson behavior.<sup>12</sup> Other work has also shown that a thin layer of cubic PBCO could be formed on the surface of an orthorhombic PBCO film by ion milling.<sup>13</sup> We also note that all-YBCO junctions have been previously produced by depositing a (perhaps cubic) YBCO interlayer at low temperatures, but these devices have been difficult to reproduce<sup>14</sup> or have displayed poor Josephson characteristics.<sup>15</sup>

Our intent is to provide only the surface of YBCO with enough kinetic energy to convert it to a different phase or structure, leaving the rest of the film in the orthorhombic state. We speculate that creation of the interlayer involves the rearrangement of Y and Ba atoms in such a way as to destroy their long-range translational order, thereby forming a quasi-cubic phase. Such a structure has been observed for YBCO films grown at low temperature.<sup>16</sup>

To create the engineered interface, we employ an *in situ* plasma treatment prior to deposition of the YBCO counterelectrode, as follows. The YBCO ramp edge is formed by our usual Ar ion milling procedure.<sup>4</sup> Immediately prior to surface treatment and deposition of the top YBCO counterelectrode, the baselayer is given an Ar ion mill clean at 500 V. The sample is then mounted in the laser deposition chamber and heated to between 400 and 600 °C in vacuum for 30 min. Next we form a plasma by biasing the heater with an rf source, using Ar and/or O<sub>2</sub> as the ionizing gas at pressures of

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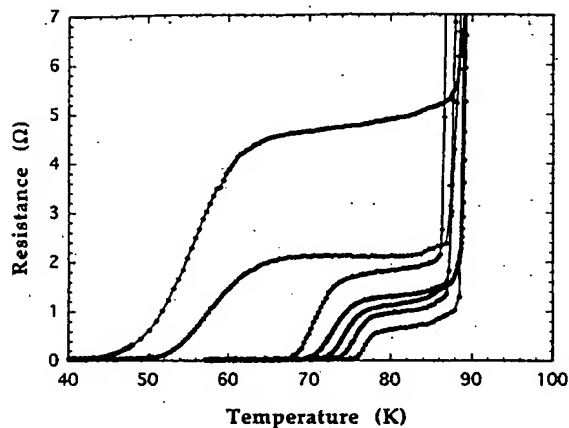


FIG. 1. The resistance vs temperature for several interface-engineered junctions with different values of  $R_n$ .

10–100 mTorr. We perform this plasma treatment for several minutes with a forward power of 100–400 W and a dc self-bias of 200–900 V. Values of the gas pressures and rf power are selected to determine the junction parameters. Following the plasma treatment, an optional further vacuum annealing step may be performed. The second YBCO layer is then deposited in the usual manner under our standard conditions. Last, these multilayered films are patterned to form five junctions per chip with cross-sectional dimensions of 4  $\mu\text{m}$  by 150 nm (the thickness of the base YBCO).

Upon cooling below the transition temperature  $T_c$  of the YBCO leads, we observe for these devices a well-defined resistance from the sharp transition at  $T_c$  down to the onset of the detectable junction critical current which occurs at a lower temperature,  $T_0$ . Figure 1 displays this behavior for several different junctions. These data indicate that the altered interface layer appears to be well localized; we observe no smeared transition or long “tail” to the superconducting state. Note that the temperature  $T_0$  varies inversely as the value of the junction resistance above  $T_0$ . This resistance is approximately equal to the value of the junction resistance  $R_n$  determined from the resistively shunted junction (RSJ)-like current-voltage ( $I$ - $V$ ) characteristics below  $T_0$ . There is also a clear inverse scaling relationship between  $R_n$  and  $I_c$ . We note that the dependence of  $T_0$  on  $R_n$  is much stronger than that for high-angle grain-boundary weak link junctions, which have a similar magnitude of  $R_n A$ . Our observed relationship may imply a different transport mechanism (or certainly a “barrier” with different properties) than that which governs high  $T_c$  grain boundaries. Electron-beam damaged junctions<sup>17–19</sup> actually exhibit a stronger relationship than ours, although their values of  $R_n A$  and  $I_c R_n$  are far lower, and they operate only over a much narrower temperature range. (Also, our junctions are completely stable at room temperature.)

Below the temperature  $T_0$  at which a critical current appears, we see  $I$ - $V$  characteristics described by the RSJ model; we have observed such  $I$ - $V$ s on each completed device of the over 350 we have measured. These RSJ-like  $I$ - $V$ s are also observed over a wide range of tunable junction parameters; for example, at 40 K,  $I_c R_n$  is adjustable between

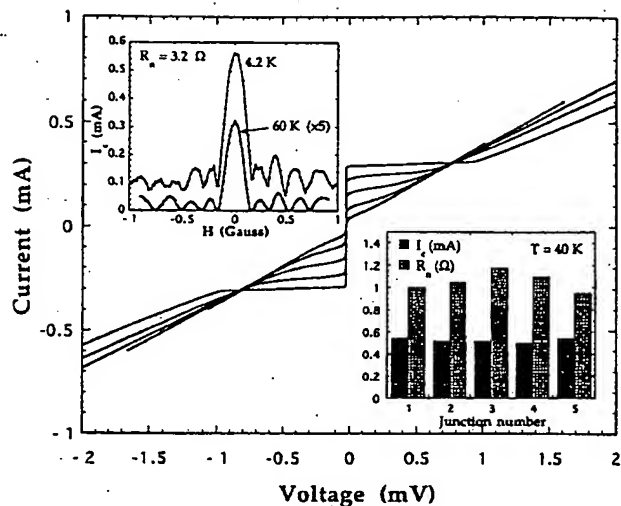


FIG. 2. Examples of the RSJ-like  $I$ - $V$  characteristics of a single junction at 4.2, 20, 30, 40, and 50 K. The insets show the magnetic field modulation of  $I_c$  for a different junction (the field is applied perpendicular to the plane of the substrate; note that the edge of the junctions is actually at an angle to this surface) and values of  $I_c$  and  $R_n$  obtained at 40 K for junctions on one of our test chips. The junction dimensions are 4  $\mu\text{m}$   $\times$  150 nm.

0.1 and 2 mV at present. Examples of the  $I$ - $V$  characteristics for a single junction at several temperatures are shown in Fig. 2. At high temperatures we often observe zero excess current and 100% magnetic field modulation (see below); at lower temperatures excess current often appears, consistent with the onset of the wide junction limit  $w > 4\lambda_J$ . However, when  $J_c$  is sufficiently small, RSJ-like behavior persists over the entire temperature range from  $T_0$  to 4.2 K. At low temperatures we sometimes observe slight hysteresis at the onset to the nonzero-voltage state. This can be attributed to a significant McCumber parameter  $\beta_c$  due to a high  $R_n$  rather than to an inordinately large junction capacitance. For junction resistances  $R_n$  of many ohms, we find that the  $I$ - $V$ s become nonlinear at high voltage bias. We have also observed this effect in high-resistance Co-YBCO grain-boundary junctions.<sup>11</sup> Thus the quasiparticle transport giving rise to  $R_n$  is not strictly metallic.

This fact is clear from the behavior of  $R_n$  with temperature. As seen in Fig. 3(a), the junction resistance tends to increase with decreasing  $T$  for  $R_n$  greater than a couple of ohms. Thus whatever the material giving rise to the resistance in our junctions is, it appears to be near some sort of metal-insulator transition. The nature of Josephson transport in this regime is not well understood, although we speculate that the existence of localized states plays a dominant role in the conduction process of these devices.

As shown in Fig. 3(b), we observe the familiar quasi-linear dependence of  $I_c$  on  $T$  as seen for most types of high  $T_c$  weak links except the Co-YBCO and Ca-YBCO SNS-type junctions<sup>5,20</sup> in which a clear exponential behavior is observed. We do not believe this behavior clarifies the nature of the weak-link effect in our junctions, and we cannot conclude that they are either “shorts” or “proximity effect” devices. In addition, we have not carefully measured  $I_c(T)$  near  $T_0$  by taking noise rounding into account, because this behavior is intrinsically nondefinitive.

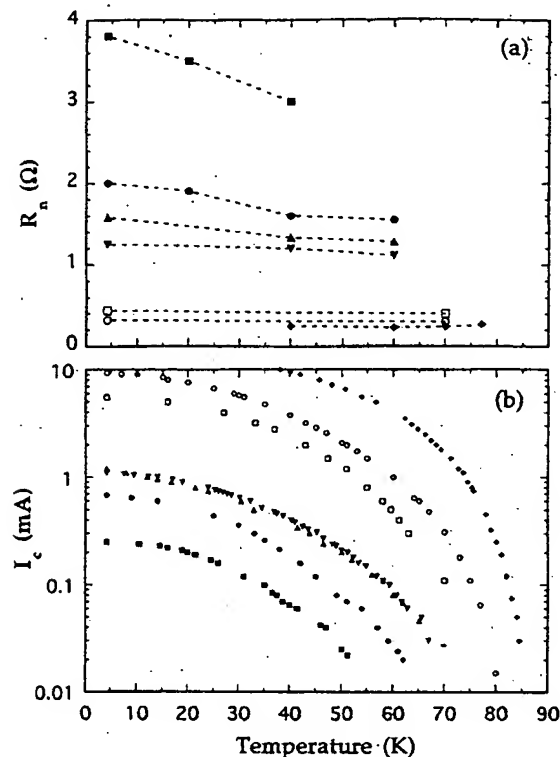


FIG. 3. Dependence of (a)  $R_n$  and (b) corresponding  $I_c$  on temperature for several different junctions.

In the inset of Fig. 2 we present an example of the behavior of  $I_c$  in a magnetic field for a  $3\ \Omega$  junction at two temperatures; a Fraunhofer-like diffraction pattern is observed.  $I_c$  is suppressed completely to zero at high temperatures and still modulates by nearly 80% at 4.2 K. The period of the  $I_c(H)$  modulation of  $\sim 0.2$  G correlates satisfactorily to the physical junction width of  $4\ \mu\text{m}$  if flux focusing is taken into account.<sup>21</sup>

In order for these devices to be useful in multi-junction circuits, junction-to-junction uniformity is required and, indeed, remains the primary hurdle to implementation of high  $T_c$  circuit technology. We believe our elimination of a deposited barrier layer will avoid many problems associated with nonuniformities. Our evaluation of over 70 five-junction test chips has demonstrated initial uniformities better than any junction technology previously pursued at Conductus. An example of the spread in  $I_c$  and  $R_n$  over five such junctions is shown in the lower inset of Fig. 2.

Finally, we mention that these junctions thus far appear to be quite stable. Their  $I_c$  and  $R_n$  values do not change over a period of several months' storage in atmosphere. Furthermore, we have annealed a  $0.5\ \Omega$  junction chip in oxygen at  $400^\circ\text{C}$  for 10 h and found that the junction parameters remain constant. These junctions even survive a high-temperature anneal at the growth temperature of  $785^\circ\text{C}$  in 400 mTorr  $\text{O}_2$  for 30 min: subsequent measurements revealed excellent RSJ behavior with a decrease of  $R_n$  and increase of  $I_c$  by about a factor of 2. Since cations begin to move at this high temperature, this result is not surprising, and we are encouraged by the fact that the junctions appear to be robust under conditions that would be used, for ex-

ample, in the subsequent deposition of ground planes, insulators, or interconnects.

To summarize, we have demonstrated a method of fabricating all-YBCO high  $T_c$  edge Josephson junctions which intentionally avoids the deposition of a barrier layer. These devices appear to be uniform and reproducible, and their electrical characteristics are easily adjustable within a range which is useful for electronic circuits. For example, an  $I_c$  of several hundred  $\mu\text{A}$  and an  $R_n$  of  $2\ \Omega$  at 40 K is ideally suited for single flux quantum technology. We note that uniformity of these ramp edge junctions may be approaching the limit achievable in this geometry (we have already measured  $1\ \sigma$  spreads in  $I_c$  lower than 8% for 10 junctions), so we deem it prudent to investigate the utility of this technique in a trilayer geometry. Finally, we stress that these junctions directly demonstrate that control of the interfaces in high  $T_c$  multilayer device technology is of paramount importance. Due to the complex nature of YBCO, deposited barrier layers of other materials in an SNS geometry are not required to achieve reliable junction operation. We believe that the properties of many SNS-type high  $T_c$  junctions are in fact dominated by the Josephson effect at the (perhaps not well-controlled) interfaces.

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# Effect of Lanthanum Doping of YBaCuO Electrodes on the Characteristics of Modified-Interface Edge Junctions

Tetsuro Satoh, Michitaka Maruyama, and Mutsuo Hidaka

**Abstract**—With the aim of improving the interface-modification process—a standard technique for forming the barrier in high-temperature superconducting Josephson junctions, lanthanum doping of a YBaCuO electrode was successfully attempted in this study. Accordingly, it was confirmed that lanthanum doping significantly affects junction characteristics; that is, it produces a lower critical current density and higher normal state resistance. In other words, lanthanum doping increased the annealing temperature or time for the barrier-formation process. These effects are advantageous for the growth of the counter layer, and for high-temperature processes made after the junction fabrication, such as upper-layer groundplane integration. It was confirmed that the lanthanum doping of the base electrode has a significant effect on the junction characteristics. It was also found that the lanthanum doping produces benefits in terms of higher critical current and normal-state resistance product.

**Index Terms**—Fabrication, high-temperature superconductors, Josephson junctions, surface treatment.

## I. INTRODUCTION

INTERFACE modification has been investigated as a process for fabricating highly uniform barriers, instead of barrier deposition or growth, for high-temperature superconducting (HTS) Josephson junctions. Moeckly and Char [1] were the first to demonstrate a reliable fabrication process for such junctions. In their fabrication process for “interface-engineered junctions” (IEJ’s), the barrier was formed on the surface of a base  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBaCuO) electrode of an edge junction by structurally modifying YBaCuO by using an argon and/or oxygen plasma treatment and vacuum annealing. The IEJ’s showed resistively and capacitively shunted junction (RCSJ)-like current-voltage ( $I$ - $V$ ) characteristics and excellent uniformity of critical current ( $I_c$ ).

Satoh *et al.* [2], [3] reported a similar kind of uniform barrier-formation process, which included amorphization by ion irradiation and crystallization by oxygen annealing, and demonstrated the possibility of larger-scale integration of modified-interface edge junctions. They showed that  $I_c$  spreads ( $1\sigma$ ) were as small as 8% for 100 edge junctions.

Recently, Soutome *et al.* [4] reported  $I_c$  spreads ( $1\sigma$ ) as small as 7.9% for 100 modified-interface edge junctions with integrated groundplanes. Other researchers also reported uniform junction characteristics [5], [6] for this kind of junction. Today, this interface-modification technique has been established as one of the most reliable barrier-formation methods for HTS Josephson junctions. It has also been studied as a fabrication process for HTS trilayer junctions [7], [8].

To improve junction characteristics and uniformity, the fabrication process of the modified-interface barrier must be further studied. For example, to maintain a barrier thickness for good junction characteristics, a growth temperature of the counter YBaCuO layer, namely the annealing temperature of the barrier, is sometimes limited to lower temperature than the appropriate values. The low growth temperature may cause incomplete epitaxial growth, or inferior superconducting properties of YBaCuO films. For making higher temperature range available for the annealing process, we were interested in a lanthanum doping of the YBaCuO electrode.

Solubility, superconducting critical temperature ( $T_c$ ), and lattice parameter of lanthanum-doped YBaCuO (La-YBaCuO) material have been studied previously [9], [10]. The maximization of  $T_c$  to 97–99 K for lanthanum doping with  $x$  of 0.05 to 0.07 was reported [9], [10]. Motivated by the higher  $T_c$  of La-YBaCuO than that of YBaCuO, Hunt *et al.* [11] used La-YBaCuO as a material for the superconducting electrodes of edge junctions. Hunt *et al.* [12] also found that  $a$ -axis grain formation was able to be eliminated, that normal state resistance ( $R_n$ ) was able to be increased, and that critical current density ( $J_c$ ) of edge junction was able to be lowered by lanthanum doping of a YBaCuO electrode. We also studied such effects on parameters in the barrier-formation process, in particular the annealing temperature or duration of the barrier. Other researchers [13], [14] also used and studied lanthanum-doped YBaCuO electrodes for edge junctions.

This paper describes our experimental results on effects of the lanthanum doping of a YBaCuO electrode on junction characteristics and on the processing parameters of modified-interface junctions. It is confirmed that the doping increases the annealing temperature and time for the barrier-formation process. The doping effect of the base electrode on junction characteristics was confirmed. It was also found that lanthanum-doped YBaCuO produces a higher  $I_c R_n$  product than that of pure YBaCuO.

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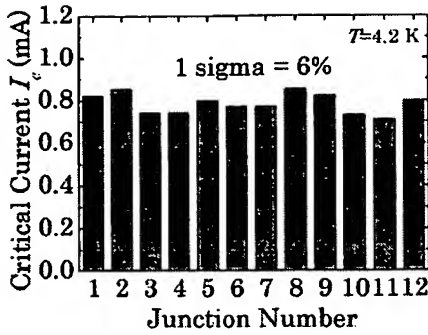


Fig. 1. Critical current ( $I_c$ ) uniformity at 4.2 K for 12 modified-interface junctions with MgO as a substrate and CeO<sub>2</sub> as an insulator layer. Both electrodes were made with pure YBaCuO. The  $1\sigma$  spread was 6% at 4.2 K.

## II. FABRICATION PROCESS

Lanthanum-doped YBaCuO films, pure YBaCuO films, and insulator films were grown by KrF pulsed laser deposition. High-density Y(Ba<sub>2-x</sub>La<sub>x</sub>)Cu<sub>3</sub>O<sub>7±δ</sub> targets were used for the lanthanum-doped YBaCuO growth, where  $x = 0.025$ , 0.05, or 0.10. Four kinds of junctions—with counter/base electrode combinations of YBaCuO/YBaCuO (Y/Y), YBaCuO/La-YBaCuO (Y/LY), La-YBaCuO/YBaCuO (LY/Y), or La-YBaCuO/La-YBaCuO (LY/LY)—were fabricated.

Modified-interface barriers were conventionally fabricated by forming a surface amorphous layer by argon-ion irradiation and crystallizing it by oxygen annealing. In the annealing process, the samples were first heated for about 25 min, during which the sample temperature rose from room temperature to the annealing temperature ( $T_{ann}$ ), and additionally heated at this temperature for an annealing duration ( $t_{ann}$ ). A counter layer was then deposited on the sample at this temperature. The full details of the fabrication process for the modified-interface junctions are given elsewhere [2], [3].

Low-dielectric constant materials, such as MgO, are usually used as substrates, and CeO<sub>2</sub> is usually used as an insulator layer. We previously confirmed that modified-interface junctions with the same RCSJ-like junction characteristics as those of previous works [2], [3], and with highly uniform characteristics, were able to be fabricated from these materials. Fig. 1 shows the uniformity in  $I_c$  of these junctions, in which both the base and the counter electrodes consist of pure YBaCuO. The uniformity ( $1\sigma$ ) in  $I_c$  was 6% for 12 junctions.

## III. RESULTS AND DISCUSSION

First we fabricated all four kinds of junctions (Y/Y, Y/LY, LY/Y, and LY/LY) by using La-YBaCuO with  $x$  of 0.05 in order to study the doping effect on junction characteristics. The annealing process parameters were the same for all samples; i.e.,  $T_{ann} = 760^\circ\text{C}$  and  $t_{ann} = 3$  min.

Fig. 2 shows  $J_c$  for these four different kinds of junctions. It is clear that  $J_c$  decreases while  $R_n$  increases by lanthanum doping of the YBaCuO electrode, as stated in previous reports [12], [14]. This effect was observed both for the doping of the counter electrode and the doping of the base electrode. However, the change in  $J_c$  for the junction doped at the base electrode is

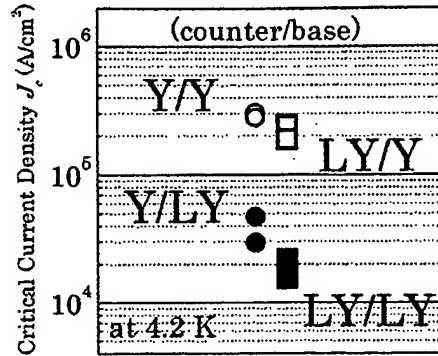


Fig. 2. Critical current density ( $J_c$ ) at 4.2 K of modified-interface junctions. Open (closed) symbols: nondoped (lanthanum doped) base electrode. Circle (square) symbols: nondoped (lanthanum doped) counter electrode. For all lanthanum-doped YBaCuO, lanthanum content  $x$  was 0.05. For all samples, annealing process parameters were same; i.e.,  $T_{ann} = 760^\circ\text{C}$  and  $t_{ann} = 3$  min.

larger than that for the junction doped at the counter electrode. The previous studies [12], [14] also pointed out the importance of the doping of the base electrode.

These measurements suggest that the presence of lanthanum during the barrier-formation process, which includes amorphization and crystallization, plays an essential role in the change in junction characteristics. Because of the small amount of lanthanum, it is unlikely that the doping will affect the amorphization. The doped lanthanum and possibly diffused lanthanum from the base electrode presumably affects the barrier-crystallization process. Lanthanum diffusion from the counter electrode to the barrier may occur and may affect the junction characteristics, but this effect is not dominant.

The dependence of the doping effect on lanthanum composition was also studied. Non-doped junctions (Y/Y), and lanthanum-doped junctions (LY/LY) with  $x$  of 0.025, 0.05, or 0.10 were fabricated under the same annealing temperature,  $T_{ann}$ , of  $760^\circ\text{C}$  and various annealing durations,  $t_{ann}$ . As shown in Fig. 3,  $J_c$  of junctions processed under the same annealing condition continuously decreases with increasing amount of lanthanum doping. This effect appears to saturate  $x$  of 0.05.

In addition, Fig. 3 shows the dependence of  $J_c$  on  $t_{ann}$ . The critical current density  $J_c$  for all junctions depends exponentially on  $t_{ann}$ , and does not saturate. The slopes for all junctions, namely, the rate of  $J_c$  increase during the annealing, are nearly the same. It can thus be that lanthanum doping only shifts the curves; it does not change their slope.

In other words, lanthanum doping enabled higher  $T_{ann}$  or longer  $t_{ann}$  in the annealing process for the same  $J_c$ . In our experiment, the lanthanum doping with  $x$  of 0.05 enabled about  $50^\circ\text{C}$  higher  $T_{ann}$  for the same  $t_{ann}$ , or about 6 min longer  $t_{ann}$  for the same  $T_{ann}$ . These are advantageous for the fabrication process of HTS integrated circuits, for example, the growth of the counter layer, and high-temperature processes made after the junction fabrication, such as upper-layer groundplane integration.

To reveal how lanthanum doping affects the barrier properties, we analyzed the junction parameters. For example, we

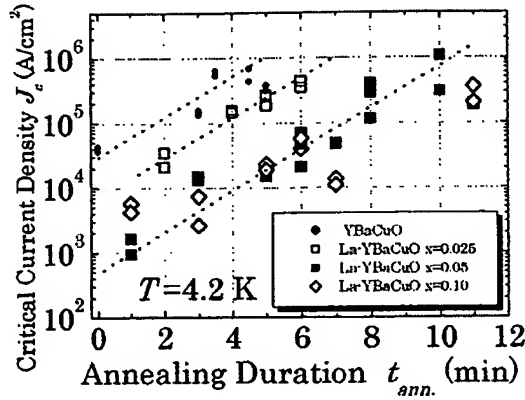


Fig. 3. Dependence of critical current density ( $J_c$ ) at 4.2 K on the annealing duration  $t_{ann}$ . For YBaCuO junctions (closed circle), pure YBaCuO was used for both the base and the counter electrode. For lanthanum-doped YBaCuO junctions,  $Y(Ba_{2-x}La_x)Cu_3O_{7\pm\delta}$  was used for both the base and the counter electrode, but lanthanum content ( $x$ ) was different; 0.025 (open square), 0.05 (closed square), or 0.10 (open diamond) for each junction. Annealing temperature was the same for all samples; i.e.,  $T_{ann} = 760^\circ\text{C}$ . The dotted lines are just guides for the eye.

TABLE I  
COMPARISON OF JUNCTION PARAMETERS

| Electrode      | $YBa_2Cu_3O_{7-\delta}$ | $Y(Ba_{2-x}La_x)Cu_3O_{7\pm\delta}$ |
|----------------|-------------------------|-------------------------------------|
| $I_c$          | 14 $\mu\text{A}$        | 15 $\mu\text{A}$                    |
| $R_n$          | 33 $\Omega$             | 62 $\Omega$                         |
| $I_c R_n$      | 0.46 mV                 | 0.93 mV                             |
| $\beta_c$      | 1                       | 1.7                                 |
| $C$            | 19 fF                   | 9.7 fF                              |
| $d/\epsilon_r$ | 1.1 nm                  | 2.2 nm                              |

compared two junctions, which have nearly the same  $I_c$  but were processed different conditions; namely,  $T_{ann}$  of  $720^\circ\text{C}$  for the nondoped junction (Y/Y),  $T_{ann}$  of  $760^\circ\text{C}$  for the lanthanum-doped junction (LY/LY). Estimated junction parameters were summarized in Table I. The normal state resistance of the doped junction ( $R_n$ ) is twice that of the nondoped junction; consequently, the  $I_c R_n$  product is as twice as large. This high  $I_c R_n$  product is one of the advantages of lanthanum doping.

We estimated the McCumber parameter ( $\beta_c$ ) from hysteresis of the  $I$ - $V$  curves for the junctions described above. Parameters  $\beta_c$ ,  $I_c$ , and  $R_n$  were used to calculate capacitance of junction ( $C$ ), and the ratio of barrier thickness to relative dielectric constant ( $d/\epsilon_r$ ). In spite of higher  $T_{ann}$  for the lanthanum-doped junction,  $I_c$  is the same as that of the pure YBaCuO junction, but the barrier thickness for the lanthanum-doped junction is larger, if  $\epsilon_r$  is unchanged by the doping.

As described above, the lanthanum doping presumably affects the barrier crystallization process. The estimated junction parameters suggest that the lanthanum doping suppresses the decrease in the barrier thickness during the crystallization process.

#### IV. SUMMARY

We studied lanthanum doping of a YBaCuO electrode with the aim of improving the fabrication process of modified-interface junctions. It was confirmed that lanthanum doping affects junction characteristics in terms of lower  $J_c$  and higher  $R_n$ . In other words, regarding the barrier-formation process, lanthanum doping enabled annealing at higher temperature or for longer duration. These are two advantageous for the growth of the counter layer and for the high-temperature processes, such as upper-layer groundplane integration, performed after junction fabrication. It was confirmed that the doping of the base electrode has a significant effect on junction characteristics. Moreover, it was found that the higher  $I_c R_n$  product is a benefit of the lanthanum doping for the switching speed of the junctions.

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